Precipitation of Heavy Metals Using *"Cuttlebone-Citrus Aurantifolia"*(CB-CA®)

by

Ahmad Azfar Bin Aziz

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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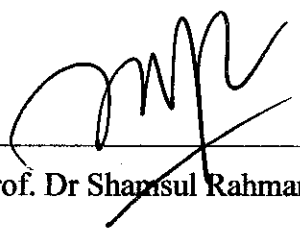
Approved by.



(Assoc. Prof. Dr Shamsul Rahman Mohamed Kutty)

Universiti Teknologi PETRONAS
Tronoh, Perak

January 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AHMAD AZFAR BIN AZIZ

ABSTRACT

This project presents the research on heavy metals removal from aqueous solution by chemical precipitation using low cost coagulant which could be used as an alternative approach to remove heavy metals from water. The low cost coagulants that are used in removing heavy metals in aqueous solution were CB which stand for cuttlebone and CA which stand for (*Citrus Aurantifolia)* or also known as key lime.

The optimum pH and optimum volume of coagulants were varied for each metals and it was depend on the characteristics of the heavy metals treated and were determined from several jar tests performed through out this project. To obtain the optimum pH, the pH of the solutions was set at increased from acidic to alkaline by adding the CB-CA solution. Each beaker was added 150 ml of heavy metals and stirrer was operated at 60 rpm for 1 minute for a rapid mix. Then, the rpm was decreased to 20 rpm for slow mix for 20 minutes. After 20 minutes, stirrer was turn off and settling was allowed for 20 minutes. The solution then was filtered to remove the remaining particles that did not settle at the bottom of the beaker. The volumes of the CB-CA solution added were recorded. Once the optimum pH was obtained, the optimum volume of CB was determined by varying the volume added at the optimum pH level. The volume that results in the most removal was identified as the optimum volume for the coagulant tested.

The result from this research shows that the CB solution had removed about more than 90% of heavy metals in aqueous solution which were Copper (Cu), Zinc (Zn) and Chromium (Cr) and about more than 60% for Cadmium (Cd). The percentage removal of Copper using CB solution as coagulant was 96.3% at pH 8.1. For Zinc, the percentage removal was 93.3% at pH 9.7. For Cadmium, the percentage removal was 60.4% at pH 9.18 and for Chromium, the percentage removal was 98.8% at pH 8.85. This shows that the CB solution had a potential to become the low cost coagulant that could be the alternative approach to remove heavy metals from aqueous solution.

ACKNOWLDEGMENT

The author would like to convey his highest gratitude to his supervisor, Assoc Prof. Dr. Shamsul Rahman Mohamed Kutty, for her guidance throughout the period of this project. The compliment should also go to all Civil Engineering department lecturers and personnel for their continuous support through out the project. Last but not least, the author would like to thank his friends and colleagues for their support and motivation. Finally, the author is forever in debt to his family for their continuous support and encouragement when it was most required.

A final word of thanks to Allah for making all of this possible.

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CHAPTER 1
INTRODUCTION

1.1 Background.

Industrial activities such as mining and metal processing can lead to heavy metals contamination in surface water, ground water, or the sea, where they can enter the food chain and causing toxic effect. They are not biodegradable and tend to accumulate in living organisms, causing various diseased and disorders [1]. Recent years, intensive studies have been performed to find low-cost and effective sorption materials for heavy metals removal. In this project, the CB-CA has been used as coagulants for removing heavy metals.

CB or cuttlebone is a hard, brittle internal structure found in all members of the family *Sepiidae*, commonly known as cuttlefish. CB is composed primarily of Calcium Carbonate ($CaCO_3$). It is a chambered, gas-filled shell used for buoyancy control. The microscopic structure of CB consists of narrow layers connected by numerous upright pillars. Depending on the species, CB can be found at a depth of between 200 m and 600 m in the ocean. As such, most species of cuttlefish live on the seafloor in shallow water, usually on the continental shelf.

The CA or key lime or its scientific name is *Citrus Aurantifolia* also known as the Mexican lime, West Indian lime or Bartender's lime, has a globose fruit, 2.5-5 cm in diameter (1-2 in), that is yellow when ripe but usually picked green commercially. It is smaller, seedier, has a higher acidity, a stronger aroma, and a thinner rind than that of the more common Persian lime.

Theme of CB-CA was investigated in this study to determine whether it can precipitated the heavy metals in the aqueous solution hence become one of the low-cost and effective materials as a coagulant that can precipitated and removed heavy metals.

1.2 Problem Statement.

Heavy metals existed in the solution of water and wastewater. Heavy metals are not biodegradable and tend to accumulate in living organisms and causing various diseased and disorders. Because of their toxicity, the presence of any of heavy metals materials in excessive quantities will interfere with many beneficial uses of the water.

To remove these heavy metals, there was lot of different methods that had been used. All of the methods required high maintenance and caused a lot of money. The costs of commercial coagulant used in removing of heavy metals are high. In this project, a chemical precipitation treatment using CB-CA solution was investigated in term of their ability to remove heavy metals from contaminated aqueous solution. CB-CA solution as coagulants were much more economical compare with other coagulants because they were natural coagulants and easy to found.

1.3 Objective and Scope of Study.

The objectives of this project are:

i. To investigate the effectiveness of using CB-CA solution for treatment of heavy metals which are Cadmium (Cd), Chromium (Cr), Copper (Cu) and Zinc (Zn).

ii. To find the optimum volume of CB solution that is needed to precipitate and optimum pH of CB solution. The result will be compared to another coagulant which is Calcium Hydroxide ($Ca(OH)_2$). With this, the effectiveness of CB as coagulant in removing heavy metals can be identified.

The scope of this research is:

i. To find the percentage removal of heavy metals in the aqueous solution when using CB-CA solution as the coagulants.

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 Heavy Metals.

Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a world wide environmental problem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Mining, metal processing, textile and battery manufacturing industry were the main sources of heavy metals ion contamination. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include Cadmium (Cd), Chromium (Cr), Copper (Cu) and Zinc (Zn) [2].

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals such as Copper, Selenium and Zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metals poisoning could result, for instance, from drinking-water contamination such as from the lead pipes, high ambient air concentrations near emission sources, or intake via the food chain [3].

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down or metabolized or excreted. Heavy metals toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs [2].

2.2 Coagulation.

Coagulation is a process of stabilizing colloidal impurities, combining small particles into larger aggregates and adsorbs dissolved organic materials into the aggregates. A wide range of coagulant exists which the most common are aluminum sulfate, ferric chloride and ferric sulfate [4]. Ferrous sulfide cannot be used alone as coagulant and it must combine with other coagulant such as lime. Since many problems were associated with ferrous sulfide, ferric chloride was the iron salt used most commonly in precipitation applications [5].

There were two main types of coagulant chemicals which were primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges of particles in the water causes the particles to clump together and were always used in the coagulation or flocculation process. Coagulant aids add density to slow-settling flocs and add toughness to the flocs to ensure that they will no break up during the mixing and settling processes. They were not always required and were generally used to reduce flocculation time [5].

2.3 Influence of Ca and CO_3.

The objective of addition of calcium chloride solution into each metal solution was to establish the effect of soluble calcium on each metal removal. The experiment with calcium carbonate solution was to establish the effects of soluble carbonate on metal removal for samples with gravel plus metal solution. The results of chemical analysis on limestone that contain high amount of $CaCO_3$ show that the limestone is capable to remove heavy metals from a solution [7]. $CaCO_3$ also exist in CB and this shows that the CB has the capabilities to remove heavy metals in aqueous solution.

2.4 Mechanism of removal.

Heavy metals removal with the addition of calcium carbonate was higher than the addition of calcium chloride while gravel alone and gravel plus calcium chloride exhibited almost similar results. The presence of dissolved calcium carbonate had

increased the pH of the solution above solubility point which causes metals to precipitate as metal oxide and probably metal carbonate [4]

2.5 Metal Treatment by Hydroxide Precipitation Process.

Precipitation of metals has long been the primary method of treating metal-laden industrial wastewaters. As a result of the success of metals precipitation in such applications, the technology is being considered and selected for use in remediating ground water containing heavy metals, including their radioactive isotopes. In ground water treatment applications, the metal precipitation process is often used as a pretreatment for other treatment technologies where the presence of metals would interfere with the other treatment processes [8].

Metals precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as clarification and filtration. The process usually uses pH adjustment, addition of a chemical precipitant, and flocculation. Typically, metals precipitate from the solution as hydroxides, sulfides, or carbonates. The solubilities of the specific metal contaminants and the required cleanup standards will dictate the process used. In some cases, process design will allow for the generation of sludge that can be sent to recyclers for metal recovery [8].

In the precipitation process, chemical precipitants, coagulants, and flocculantation are used to increase particle size through aggregation. Fine particles are held in suspension by electrostatic surface charges that cause clouds of counter-ions to form around the particles, generating repulsive forces that prevent aggregation and reduce the effectiveness of subsequent solid-liquid separation processes. To overcome these repulsive forces, chemical coagulants are often added. The three main types of coagulants are inorganic electrolytes (such as alum, lime, ferric chloride, and ferrous sulfate), organic polymers, and synthetic polyelectrolytes with anionic or cationic functional groups. After the addition of coagulants, low-sheer mixing in a flocculator is necessary to promote contact between the particles, allowing particle

growth through the sedimentation phenomenon called flocculant settling whereby the particles will increase in mass and settle at a faster rate [8]

When metals enter the aqueous solution, they tend to be in stable form, dissolved and unable to form solids by their own. The objective of metals treatment by hydroxide precipitation is to adjust the pH from acidic to alkaline so that the metals will form insoluble precipitates [9]. Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged. Metals precipitation is primarily dependent upon two (2) factors which are:

i. The concentration of the metals
ii. pH of the aqueous solution

Heavy metals usually present in aqueous solution in dilute quantities which are from 1-100mg/L and usually at neutral and acidic pH values (<7.0). Both of these factors are disadvantageous with regard to metals removal. When one adds caustic to water contain dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids.

$$2Cu + Ca(OH)_2 = Cu(OH)_2 + Ca^{2+}$$

[9]

Based on experiments conducted on several metals, by simply adjusting the pH from 6.8 to 8.6 has effectively precipitated most of the dissolved metal from the water. Since all metals display similar effects, it is clear that the adjustment of pH is critical when the metal is to be removed from the wastewater. However, the metals now exist in another phase or state which is as small solid particles and must be removed typically by subsequent sedimentation and filtration processes [9].

The metals solubility curves presented in Figure 1 are based on an ideal wastewater. Some variations in the exact values of the metal concentrations will occur due to the presence of other substances in the wastewater. Compounds such as cyanide or ammonia can inhibit precipitation of metals, and limit their removal to the point where discharge limits can be exceeded. Also, it must be reminded that not all

metals have the same minimum solubility. Therefore in a wastewater where multiple metals are present, as a general rule, pH at approximately 9 should be adjusted as an average value [5].

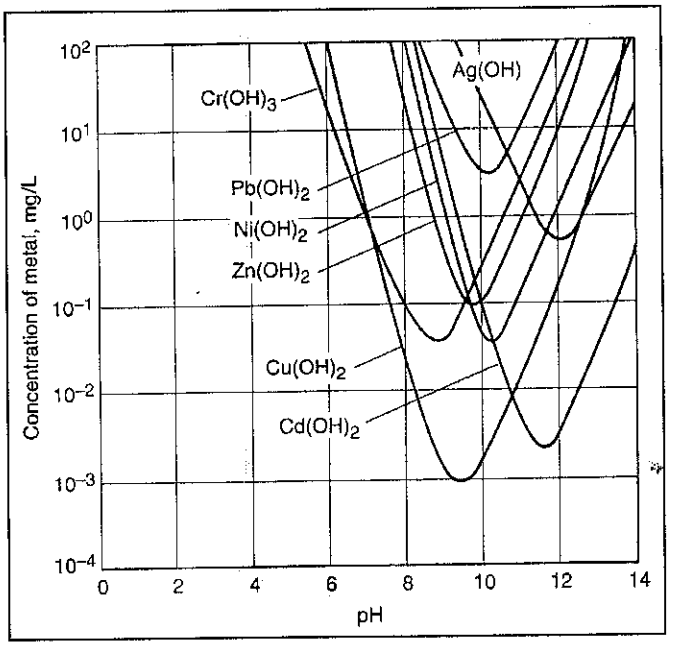

Figure 2.1: Residual soluble metal concentration as a function of pH for the precipitation of metals as hydroxides (Metcalf and Eddy, 2004).

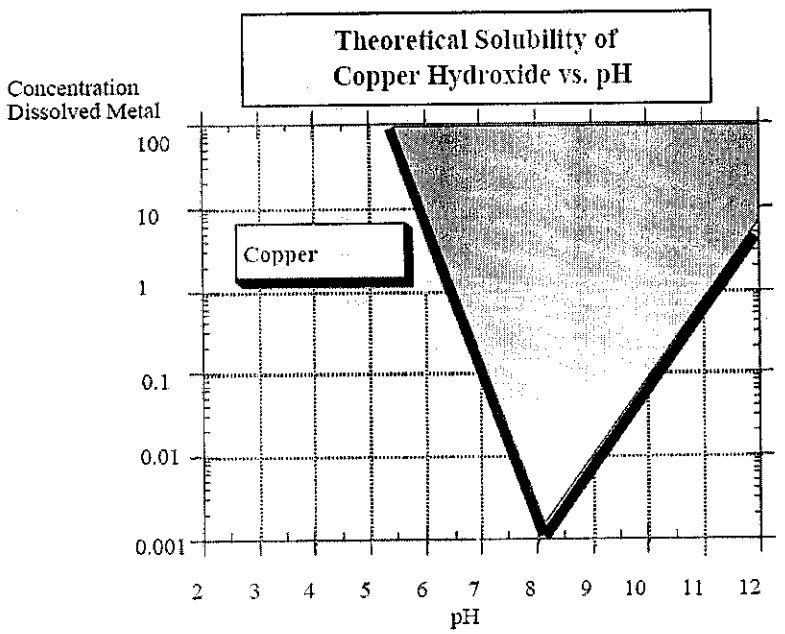

Figure 2.2: Theoretical Solubility of Copper Hydroxide VS pH (David M. Ayres et. Al., 1994).

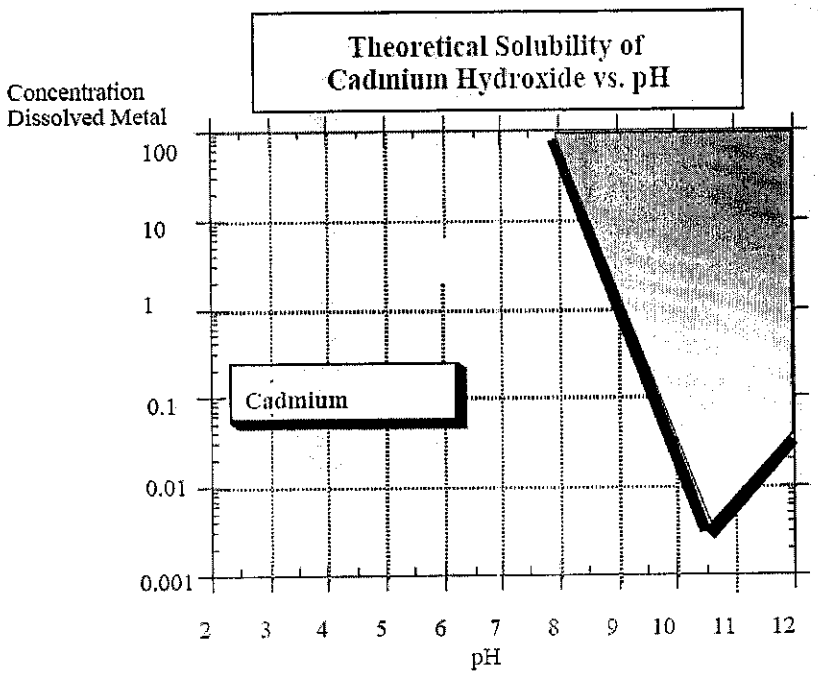

Figure 2.3: Theoretical Solubility of Cadmium Hydroxide VS pH (David M. Ayres et. Al., 1994).

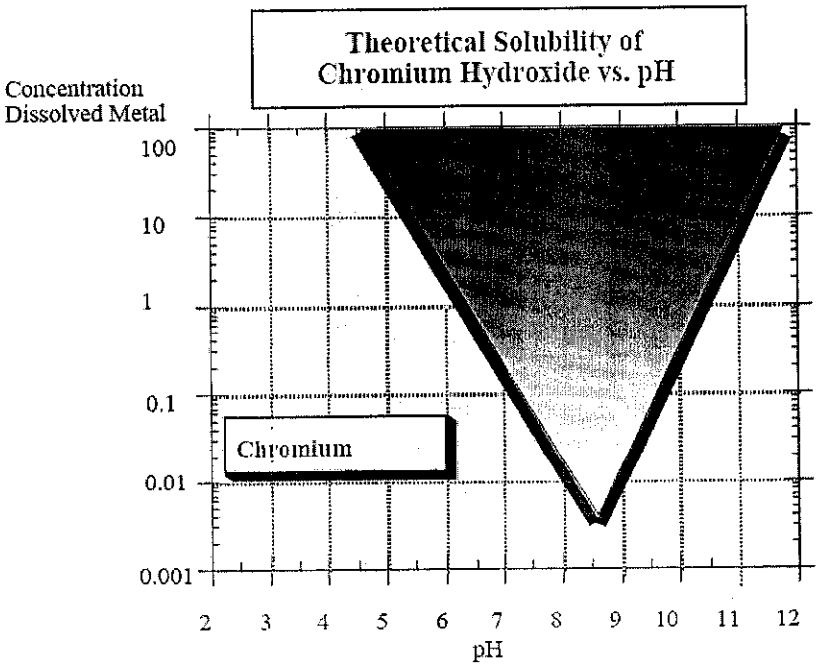

Figure 2.4: Theoretical Solubility of Chromium Hydroxide VS pH (David M. Ayres et. Al., 1994).

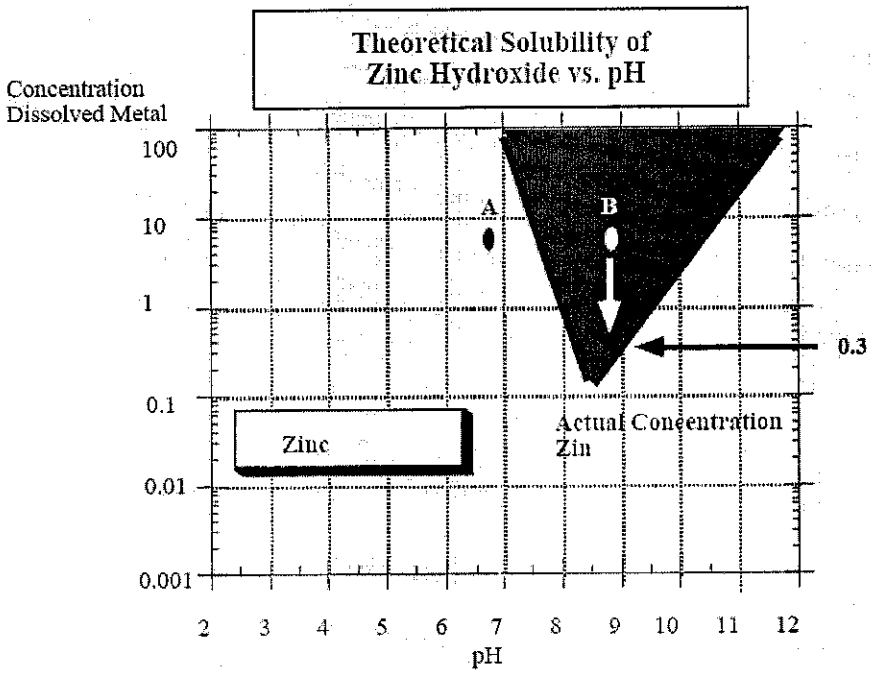

Figure 2.5: Theoretical Solubility of Zinc Hydroxide VS pH (David M. Ayres et. Al., 1994).

Figure 2.2 till Figure 2.5 shows the solubility curves of Copper, Cadmium, Chromium and Zinc. These solubility graphs or solubility curves display the regions where the metals are soluble or insoluble. The region above the dark lines for each metal signifies that the metals should precipitate as metals hydroxides. This is referred to as the precipitation region. The region below or outside of the dark lines illustrates where the metals are dissolves in solution, no precipitation occurs and no metal removal that taken place.

Figure 2.5 can be used to determine how the concentration of zinx in water is affected by pH. Suppose an aqueous zinc solution contain dissolve zinc at 4 mg/L and is at pH 6.8 (Point A). Since the point below the bold lines in the solubility curve, this indicates that zinc is only present as a dissolved metal. It is not in a solid form and under these conditions it will not precipitate. To remove zinc in this solution, the pH needs to be adjusted by adding alkaline. Point B reveals this pH adjustment from pH 6.8 to 8.6. Above the dark solubility lines, zinc will form hydroxide solids and at this new pH, the zinc will precipitate. The dissolve zinc concentration is obtain from the solubility curve at pH 8.6 is 0.3 mg/L [9].

By simple just adjusting the pH value into the range of shaded area has effectively precipitated most of the dissolved metal from the water. Since all metals display similar effects, it shows that the adjustment of pH from acidic to alkaline is critical when the metal is to be removed from the aqueous solution [9].

CHAPTER 3
METHODOLOGY

3.1 Preparation of CB Sample.

The CB was pulverized using grinding machine in concrete laboratory. A grinding machine is a machine tool used for producing very fine finishes or making very light cuts, using an abrasive wheel as the cutting device. This cutting device can be made up of various sizes and types of stones, diamonds or of inorganic materials. The CB was grinded until it becomes powder which the size of the powder was 150μm.

Then, the CB powder was dissolved in distilled water. Chemical reactions generally occurred more efficiently as surface area between the reacting chemicals was increased. By dissolving substances, the substance was breaking down into individual molecules in some cases and into individual ions in others.

Figure 3.1: Solubilization of cuttlebone.

3.2 Preparation of Heavy Metals Aqueous Solution.

To start an experiment, heavy metals aqueous solution need to be prepared. In this project, Cadmium (Cd), Chromium (Cr), Copper (Cu), and Zinc (Zn) solution have been chosen as the heavy metals solution. The concentration of these aqueous solutions should be around 10 ppm. The calculations for each heavy metal aqueous solutions were shown in the APPENDIX IV. To prepare the heavy metals aqueous solution. The steps of calculation were shown below:

i. First the chemical compound, formula weight and atomic number of heavy metals were determined.
ii. Formula weight was divided with atomic number of the chosen heavy metal.
iii. To find the weight of heavy metal that will be added to make the aqueous solution, the amount of distilled water was times with step ii.

As the calculation shown in the APPENDIX IV, certain amount of heavy metal salts was dissolved into certain amount of distilled water. To make sure the concentration of heavy metals solution, 3 samples of each solution was tested by using Atomic Absorption Spectrophotometer (AAS). The result from AAS test shows that the concentration of these heavy metals solutions was around 8 ppm to 10 ppm.

3.3 X-Ray Fluorescence Technique (XRF).

A sample from cuttlebone and key lime had was to mechanical laboratory for checking their elements and compound. To check the elements and compound of each sample, XRF technique had been used. This experiment had been conducted by laboratory staff because it using X-ray technique.

X-Ray fluorescence (XRF) is a quantitative elemental analysis technique based on the characteristic X-ray emission behavior of different elements under incident X-ray irradiation. When supplied with high energy radiation (e.g. X-ray), an electron is knocked out of its shell, and replaced with an electron from a higher energy shell. This high-low energy transition results in the emission of photons, the set of wavelengths for which is specific to each element. Examination of relative

intensities of different emitted wavelengths can thus give a quantitative measurement of relative quantities of each element in a sample.

3.4 Jar Test Procedure.

Jar test laboratory equipment used to determine the optimum operating condition for water and wastewater treatment. The equipment allowed adjustment in pH, variation in coagulant, polymer dose and alternating mixing speed. Different coagulant or polymer types can also be tested on a small scale in order to predict the functioning of a large scale treatment operation. A jar test stimulates the coagulant and flocculation processes that enhanced the removal of suspended colloids and organic matter which can lead to turbidity, odor and taste problem.

To precipitate heavy metals, the pH of heavy metals solution needs to be adjusted from acidic to alkaline. In this research, to adjust the pH of heavy metals solution to be acidic, the *Citrus Aurantifolia* (CA) and hydrochloric acid (HCl) were used. To make the solution to become alkaline, cuttlebone (CB) and Calcium Hydroxide $Ca(OH)_2$ were used. Jar test was be done by using beakers, magnetic stirrers and stir bar. These 3 equipments were used in the jar test equipment. In each beaker, 150 mL of heavy metal aqueous solution to was added. The magnetic stirrer was operated at 60 rpm for approximately 1 minute. This stimulates the static mixer. During this rapid mix, CB-CA was added to adjust the pH of the heavy metal aqueous solution. After all the 6 beakers have been adjusted, the rpm was decreased until it matches the turbulence created in the flocculators (20 rpm) and stirring was allowed for 25 minutes while the floc formation was observed. After 25 minutes, the stirrer was turned off and settling was allowed for 20 minutes.

Jar test was prepared for CB solution and Calcium Hydroxide, $Ca(OH)_2$. The pH for each solution in the jar was adjusted, ranging form pH 2 to pH 10 by adding CA to make the aqueous solution to be acidic and CB solution and Calcium Hydroxide, $Ca(OH)_2$ to be alkaline. After 20 minutes, each aqueous solution had been filtered. The purpose of this filtration was to trap those particles that did not settle in the bottom of the beakers or did not have sufficient time to settle and were carried out of the basin

3.5 Measurement of Heavy Metals.

After the filtration processes, the solution will be tested for the concentration of heavy metals that contain in the filtered solution by using the atomic absorption spectrophotometer (AAS). AAS provides accurate quantitative analyses for metals in water, sediments, soils or rocks. (Samples are analyzed in liquid form, so solid samples must be leached or dissolved prior to analysis.).

Before starting to use AAS, a standard need to be prepared for each heavy metal. Standard solutions need to be prepared of at least three different concentrations which were 1 ppm, 3 ppm and 5 ppm. and then the absorbance of these standard solutions had been measured, and a calibration curve from the obtained values had been prepared. Then measures the absorbance for the test solution adjusted in concentration to a measurable range, and determine the amount (concentration) of the object element from the calibration curve. After the standard had been prepared, 3 samples of raw heavy metal aqueous solution and 3 samples taken from each beaker were measured using AAS. The graph of heavy metal concentration VS pH was plotted. The pH with the minimum heavy metals concentration was considered as the optimum pH.

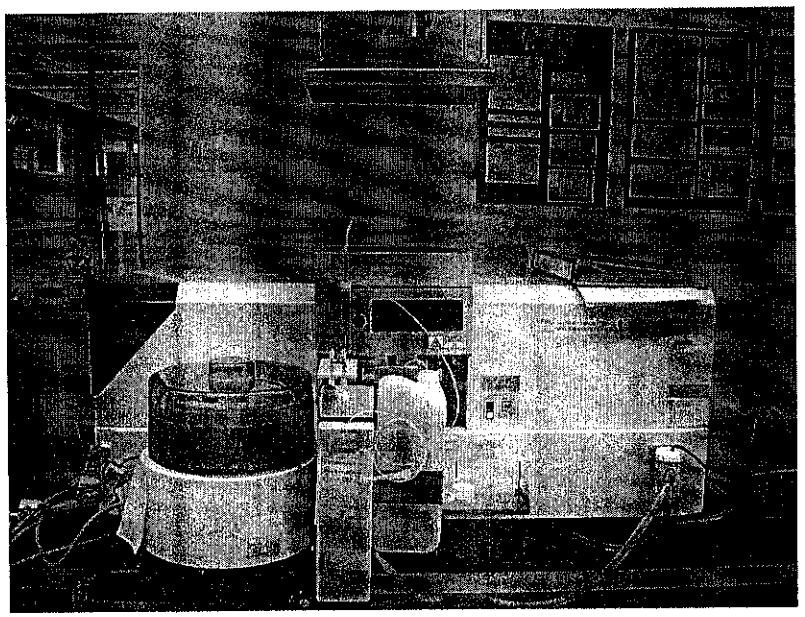

Figure 3.2: Atomic Absorption Spectrophotometer (AAS) machine.

3.6 Hazard Assessment.

Hazard is defined as anything that can cause harm or damage such as chemical reaction and other hazardous material. Dealing with the heavy metals in the laboratory, some protection needs to be used because heavy metals are a hazardous material. The laboratory hazard assessment identifies hazards to students and specifies PPE (Personal Protective Equipment) to protect students during work activities. Before entering the environmental laboratory, there was a briefing by technician about hazard assessment. There were a lot of requirements that need to be done when students entered the laboratory. The requirements were:

i. Conduct a hazard assessment of the laboratory to identify activities where PPE is needed to protect the students from exposure to hazards.

ii. Specify the PPE to be used by the students to protect from the hazards identified such as wearing the laboratory coat and chemical-resistant glove.

iii. 'Certify' the hazard assessment for the laboratory.

When conducting this project, the potential hazards had been determined. The table below shows the potential hazards in the environmental laboratory while conducting this project.

Chemical used Hazards		
Activity	Potential Hazard	Recommended PPE
Working with small volumes of corrosive liquids (< 1 liter).	Eye or skin damage	Safety glasses or goggles Light chemical-resistant gloves, Lab coat
Working with toxic or hazardous chemicals (solid or liquid).	Eye or skin damage; potential poisoning through skin contact.	Safety glasses (goggles for large quantities) Light chemical-resistant gloves, Lab coat
Working with an apparatus with contents under pressure (such as distillation) or highly reactive materials	Eye or skin damage	Safety glasses or goggles (consider face shield), appropriate chemical-resistant gloves, lab coat.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 X-Ray Florescence Technique (XRF).

CB-CA sample were taken to Mechanical Laboratory to check for their element and composition and finally the result for the test had come out (Refer APPENDIX I). The result was only for CB sample because for the CA sample, the X-ray Fluorescence Technique (XRF) cannot be done because the sample was in a liquid form. To perform this XRF test, the sample needs to be in a solid form. The result for XRF test that had been conducted at Mechanical Laboratory was shown below:

Compound	Content	Percentage %
Na_2O	3.9 KCps	1.75
MgO	1.8 KCps	0.277
Al_2O_3	0.8 KCps	0.148
SiO_2	1.7 KCps	0.246
P_2O_3	0.7 KCps	0.103
SO_3	5.5 KCps	0.474
Cl	27.5 KCps	2.13
K_2O	3.1 KCps	0.132
CaO	1464.2 KCps	92.8
Fe_2O_3	2.5 KCps	0.00564
CuO	3.8 KCps	0.0061
SrO	200.1 KCps	0.977
ZrO_2	40.0 KCps	0.0224
Re	18.2 KCps	0.705

Table 4.1: XRF Result of Compound Component for Cuttlebone.

Element	Content	Percentage %
O	0 KCps	27.4
Na	3.9 KCps	1.30
Mg	1.8 KCps	0.167
Al	0.8 KCps	0.0783
Si	1.7 KCps	0.115
P	0.7 KCps	0.0448
S	5.5 KCps	0.190
Cl	27.5 KCps	2.13
K	3.1 KCps	0.109
Ca	1464.2 KCps	66.3
Fe	2.5 KCps	0.00394
Cu	3.8 KCps	0.00487
Sr	200.1 KCps	0.826
Zr	40.0 KCps	0.0166
Re	18.2 KCps	0.705

Table 4.2: XRF Result of Element Component for Cuttlebone.

By referring to table 4.1 and table 4.2, the result of XRF test had shown that the most elements that exist in the CB were calcium (Ca). Calcium compound and its element have 1464.2 KCpa compare to the other element. KCpa stand for Kilo Crypt-equivalent-operations Per Second and it is a sensitivity measurement of the machine in kilocycles per second. Calcium was one of the elements that can precipitate heavy metals. So, the existing of Calcium in CB shows that the CB has a potential to precipitate heavy metals. If CB can exactly precipitate heavy metals, it can be used world wide as one of the coagulant that can precipitate heavy metal.

4.2 Precipitation of Cu^{2+} Aqueous Solution.

Heavy metals were precipitated by adding alkaline compounds such as Sodium Hydroxide (NaOH), Calcium Hydroxide ($Ca(OH)_2$), Sodium Carbonate (Na_2CO_3) and Calcium Carbonate ($CaCO_3$) [10]. The element of CB was Calcium and the compound was Calcium Carbonate ($CaCO_3$). An experiment had been conducted to remove Copper from aqueous solution by finding the optimum pH. The optimum pH for removal of Copper by using CB and Calcium Hydroxide ($Ca(OH)_2$) were obtained through the jar test (Refer APPENDIX II). For the first jar test, CB was

used as a coagulant while in the second jar test; Calcium Hydroxide ($Ca(OH)_2$) was use as a coagulant. Both results were shown in Figure 4.1 below:

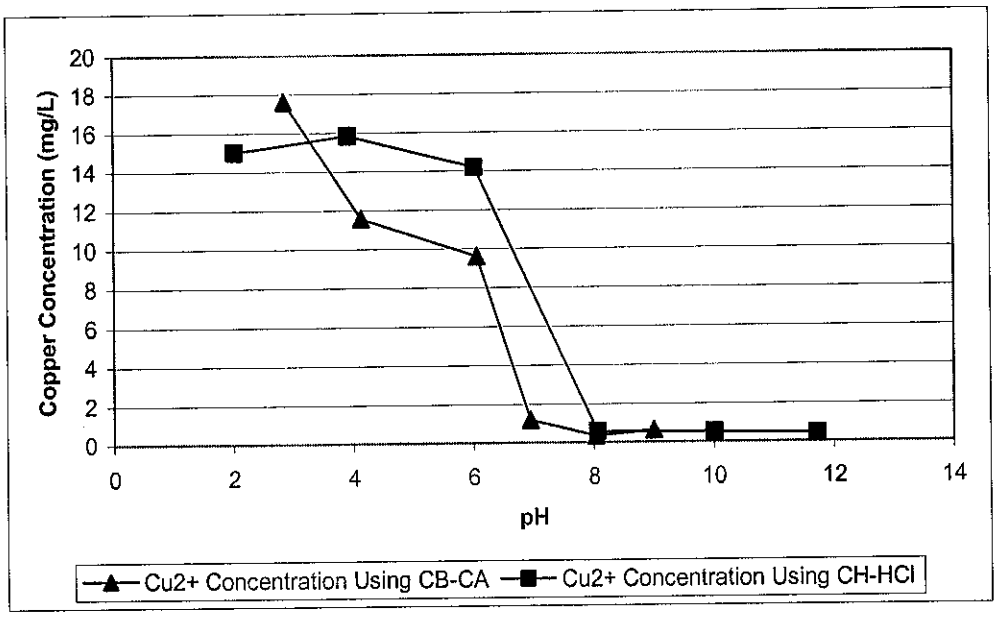

Figure 4.1: Residual Copper Concentration VS pH. [C_o = 17.2 ppm, pH_o =3.24]

The initial raw of copper solution was 17.2 ppm and the initial pH was 3.24. In the first jar test, CA has being used to set the initial pH of the Copper solution to be acidic and CB to become alkaline. In the second jar test, Hydrochloric Acid (HCl) had being used to make the initial pH to become acidic while the calcium hydroxide ($Ca(OH)_2$) was used to make the Copper solution to become alkaline. As the jar test had finished, the solution had been allowed to settle about 20 minutes and after that, it had been filtered using syringe filter. The solution or the sample had been tested for Copper concentration by using atomic absorption spectrophotometer (AAS) (Refer APPENDIX II).

From Figure 4.1, by using the CB solution as the coagulant, the result seems to be correct because the Copper concentration was decreased when the pH increased from acidic to alkaline. By referring to the research wrote by David M. Ayres et al. (1994), (Refer Figure 2.2) the solubility curve of Cooper removal was likely the same as the graph in Figure 4.1. The optimum pH of removal Copper by using CB was 8.1 which were exactly the same which was stated in the research. The graph in Figure 4.1 shows that Copper concentration decreased until pH exactly 8.1. Then the copper concentration was increased as the pH increased.

Still referring to Figure 4.1, the Calcium Hydroxide ($Ca(OH)_2$) was used as a coagulant, the graph shows that the Copper concentration decreasing as the pH value increasing. Same as CB, the optimum pH of Copper removal was 8.1. Calcium Hydroxide ($Ca(OH)_2$) was used to compare with CB. This because, both solution having Ca^{2+} in each solution. By comparing, the results it was more effective because by comparing, whether the result of CB solution as a coagulant can remove heavy metals was correct or not.

Both graph shows the decreasing of copper concentration as the pH increased and providing optimum pH of 8.1 for CB and calcium hydroxide ($Ca(OH)_2$) as a coagulant. However, from the copper solubility curve by Metcalf and Eddy (2004), the optimum pH for copper to be removed was pH 9.4.

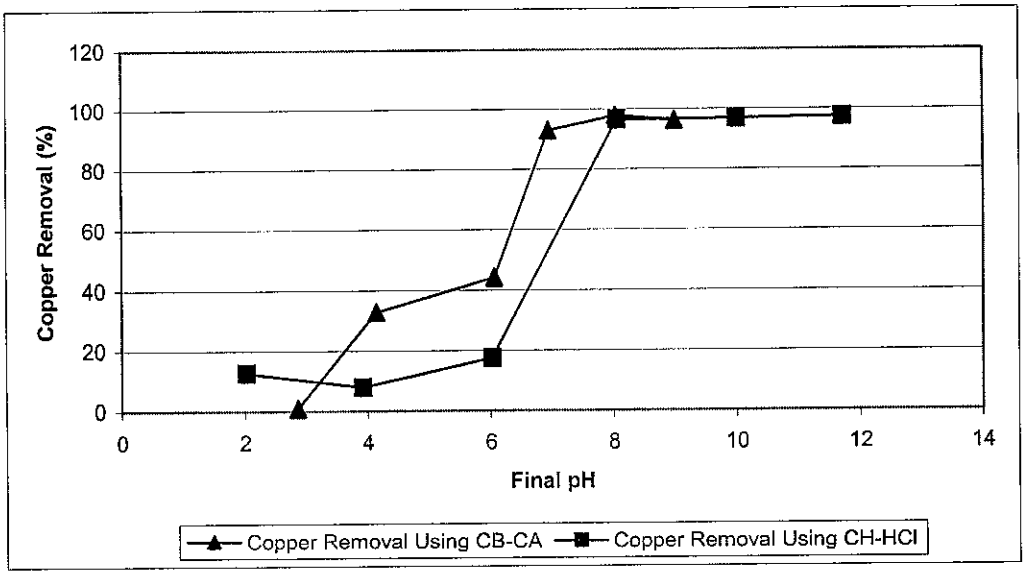

Figure 4.2: Percentage of Copper removal against final pH.

Figure 4.2 shows plot of copper removal against pH. The result of Copper removal using CB solution and Calcium Hydroxide ($Ca(OH)_2$) was shown above. By comparing those two coagulants, both have removed more than 90% of Copper in the aqueous solution. The percentage of copper removal by CB was about 96.3% while the calcium hydroxide ($Ca(OH)_2$)had removed Copper about 97.5%. Both removal of Copper was as pH of 8.1.

4.3 Precipitation of Zn^{2+} Aqueous Solution.

Zinc solution was obtained by dilution of 416.73 mg of zinc salt into 20 liter of distilled water. The legal limit for discharging water that contains Zinc into a river or sea is 1.0 mg/L which was stated under Malaysian-Environment Quality Act 1974 [7]. So, in this research, an experiment has been conducted to find the optimum pH of Zinc removal to remove Zinc in the aqueous solution. The procedure for conducting this experiment was similar as conducting the experiment for Copper removal. (Refer APPENDIX II for Jar Test Result of Zinc Removal). Both results were shown in Figure 4.3.

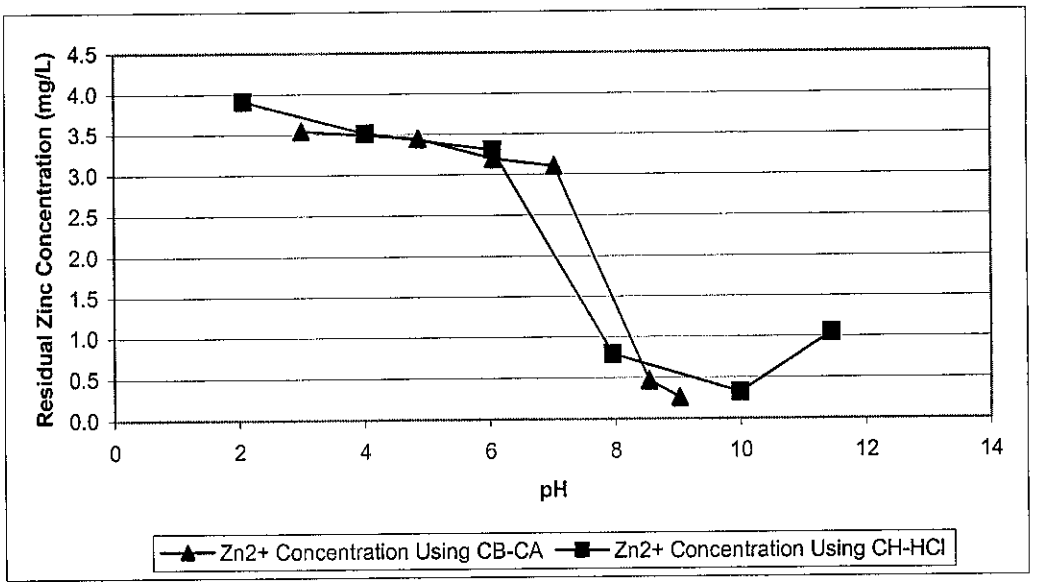

Figure 4.3: Residual Zinc Concentration VS pH. [C_o = 3.95 ppm, pH_o =4.46]

The initial pH and concentration of zinc solution were 4.46 and 3.95 ppm. For the first graph, the Zinc concentration decreased as initial pH increased. The optimum pH for Zinc removal was approximately 9 when using CB as a coagulant. For the second graph, by using the Calcium Hydroxide ($Ca(OH)_2$ as a coagulant, the Zinc concentration decreased until it reaches the optimum pH of 10. After pH 10, the Zinc concentration increased or in other way, the Zinc has not been precipitated after the optimum pH of 10. The theoretical solubility curve stated by Metcalf and Eddy (2004), the optimum pH for Zinc was in the range of 9.7. But, David M. Ayres et al (1994) (Refer Figure 2.5) had stated in his research that the optimum pH in removing Zinc was at pH 8.5. The optimum pH for Zinc was different but still the

range of Zinc removal was from 7 to 11. So, by right, both graph of Zinc concentration using CB solution and Calcium Hydroxide ($Ca(OH)_2$) was right. By simply adjusting the pH from 7 to 11 has effectively precipitated most of the dissolved metal from water.

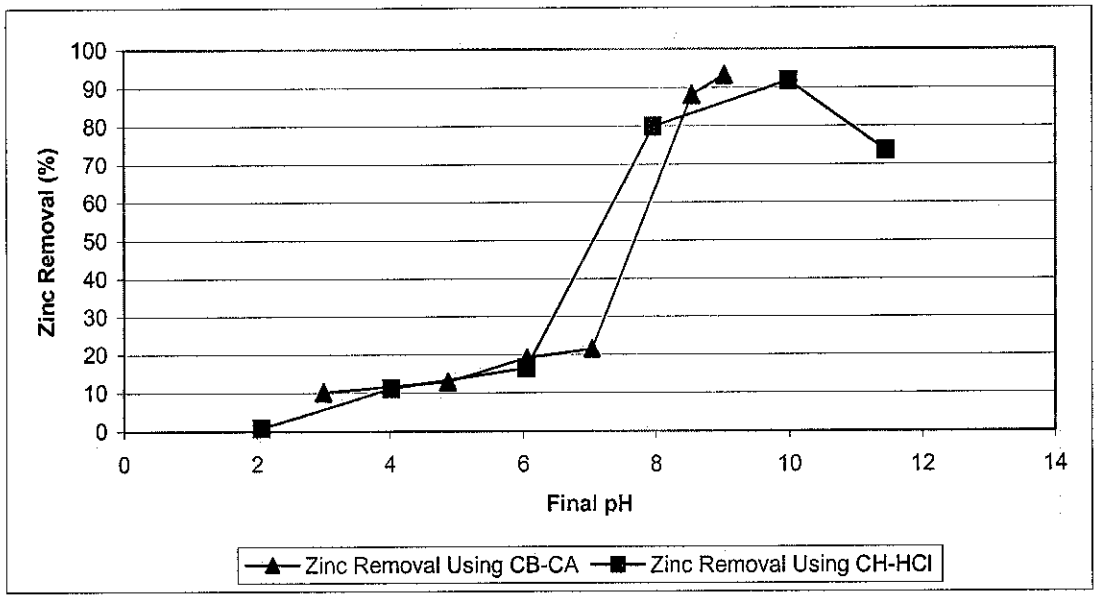

Figure 4.4: Percentage of Zinc removal against final pH.

The graph in Figure 4.4 above shows the Zinc percentage removal using CB solution and Calcium Hydroxide ($Ca(OH)_2$). By comparing this two coagulants, the result of removal of Zinc by using CB solution and Calcium Hydroxide ($Ca(OH)_2$) was clearly seen because the both coagulants have removed more than 90% of Zinc metal in the Zinc aqueous solution at pH 9. The percentage (%) of Zinc removal by using CB solution was 93.3% and Calcium Hydroxide ($Ca(OH)_2$) was 91.8 at % at pH 10.

4.4 Precipitation of Cd^{2+} Aqueous Solution.

Besides Copper and Zinc, Cadmium also one of the heavy metals that contain in the water. The maximum limit under the standard B discharge limit under Malaysian-Environmental Quality Act 1997 (Sewage and Industrial Effluents) 1979 is keep below 0.02 mg/L for cadmium [7].

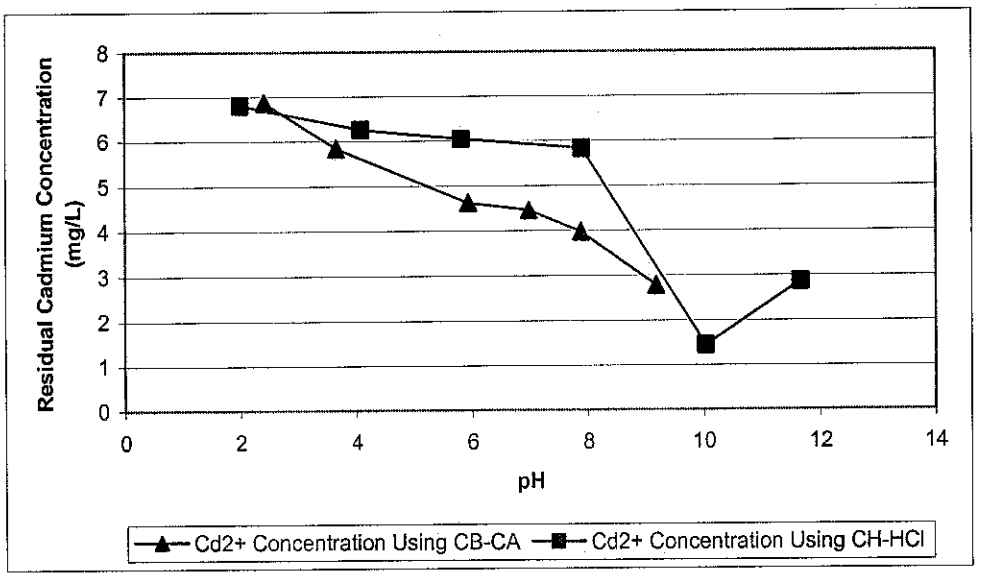

Figure 4.5: Residual Cadmium Concentration VS pH. [C_o = 7.04 ppm, pH_o =2.48]

The initial pH and concentration of Cadmium solution were 2.48 and 7.04 ppm. From Figure 4.5, the concentration of Cadmium were decreased when CB solution and Calcium Hydroxide ($Ca(OH)_2$) were used as the coagulant. By referring the solubility curve in Figure 2.1, the optimum pH that was stated by Metcalf and Eddy (2004) was 11.5. By referring to the research wrote by David M. Ayres et al. (1994), the solubility curve of Cadmium removal where the optimum pH of Cadmium was at the pH 10.5 (Refer Figure 2.3).

By using CB solution as a coagulant, the maximum pH that can obtain from CB solution was in the range of pH 9 – pH 9.4. As the result, the graph of Cadmium concentration using CB solution cannot reach the optimum pH removal of Cadmium. But, the analysis or measurement by using Atomic Absorption Spectrophotometer (AAS) shows that, the concentration of cadmium in the Cadmium aqueous solution was decreasing. To compare the CB solution, Calcium Hydroxide ($Ca(OH)_2$) had been used as a coagulant. From Figure 4.5, the graph of Cadmium concentration using Calcium Hydroxide ($Ca(OH)_2$) was shows that the optimum pH in removal of Cadmium was 10.1.

The result using Calcium Hydroxide ($Ca(OH)_2$) as a coagulant still not the same as the past researcher (Metcalf and Eddy (2004) and David M. Ayres et al. (1994)) had stated. But the optimum pH using Calcium Hydroxide ($Ca(OH)_2$) was in the range

of Cadmium removal. Both researcher stated that the solubility curve of Cadmium removal were in the range of pH 8 to pH 14. So, as the Cadmium aqueous solution becomes alkaline of pH more than 8, most of the Cadmium metal was precipitated.

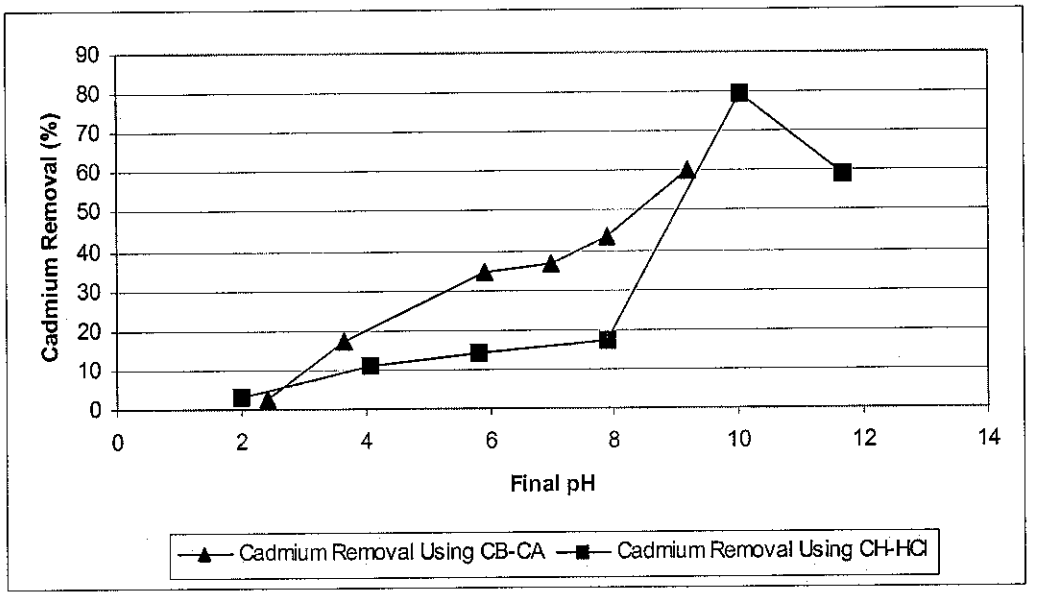

Figure 4.6: Percentage of Cadmium removal against final pH.

From figure 4.6, the graph shows the percentage of Cadmium removal again final pH by using CB solution and Calcium Hydroxide ($Ca(OH)_2$). By comparing this two coagulants, the result of removal of Cadmium by using CB solution and Calcium Hydroxide ($Ca(OH)_2$) was clearly seen because the both coagulants have removed Cadmium metal in the Cadmium aqueous solution. The removal of Cadmium by using CB solution was low compare to Calcium Hydroxide ($Ca(OH)_2$). The maximum pH of CB solution was 9.4, thus it cannot reach the optimum pH of removal Cadmium in the aqueous solution and as the result, the percentage of removal Cadmium was low compare to the other coagulant which was Calcium Hydroxide ($Ca(OH)_2$). The percentage (%) of Cadmium removal by using CB solution was 60.4% at pH of 9.14 and Calcium Hydroxide ($Ca(OH)_2$) was 79.4% at pH of 10.

4.5 Precipitation of Cr^{2+} Aqueous Solution.

The last heavy metals that were tested in this project were Chromium. The legal limit for discharging water that contains Chromium into river or sea is 1.0 mg/L. This limit is a standard B discharge limit under Malaysian-Environmental Quality Act 1974 [7]. An experiment has been conducted to find the optimum pH of Chromium removal to remove Chromium from aqueous solution. The procedure was the as the other heavy metals that had been conducted before (APPENDIX II had shown the result of Chromium removal).

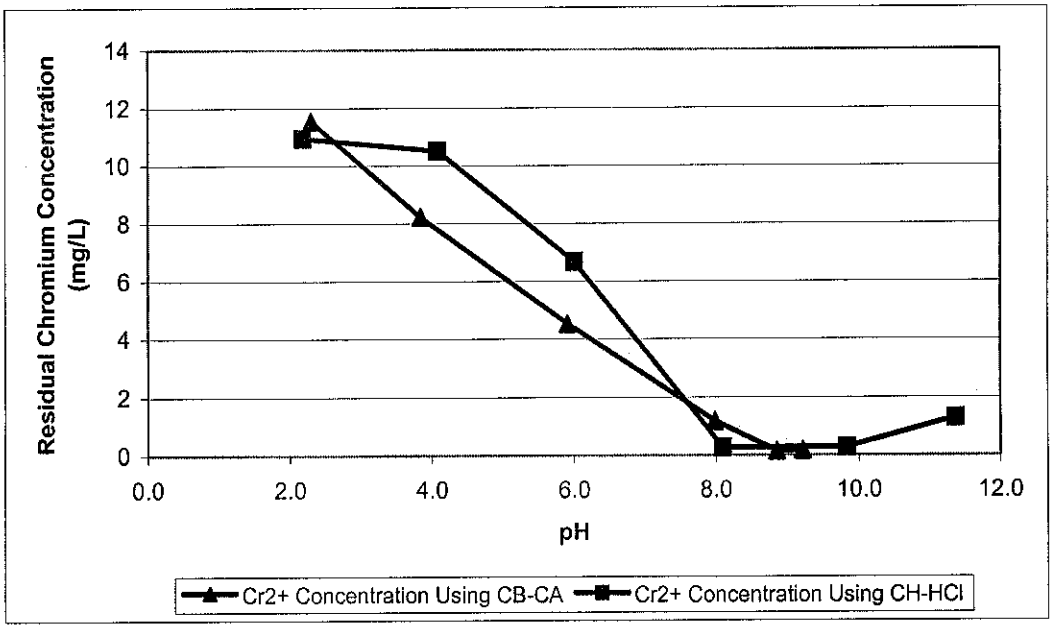

Figure 4.7: Residual Chromium Concentration VS pH. [C_o = 12.01 ppm, pH_o =2.73]

The initial pH and concentration of Chromium solution were 2.73 and 12.01 ppm. Figure 4.7 had shown the Chromium concentration VS final pH. There were two (2) coagulants that have been used in conducting this experiment. The procedure of conducting the experiment was the same as previous experiment. In Figure 2.1, the optimum pH for Chromium which was stated by Metcalf and Eddy (2004) was 8.8. The solubility curve that shown in the research paper which was wrote by David M. Ayres et al (1994) shows that the optimum pH for Chromium removal was 8.6.

By referring to Figure 4.7, the first graph which was using CB solution as a coagulant shows that the concentration of Chromium was decreased as the increasing of pH values. The optimum pH of Chromium removal was 8.85. After

the Chromium reached the optimum pH, the concentration of Chromium increased as the pH value increased. For the second graph, Calcium Hydroxide ($Ca(OH)_2$) had been used as the coagulant to remove Chromium in the aqueous solution. The optimum pH of Chromium when using Calcium Hydroxide ($Ca(OH)_2$) as coagulant was 8.96. The theoretical solubility curve by Metcalf and Eddy (2004) and David M. Ayres et al (1994) stated that the range of Chromium removal were from pH 6 to pH 12. As the results that shows from both coagulants which were CB solution and Calcium Hydroxide ($Ca(OH)_2$), the optimum pH of both results were slightly different between each other and slightly different with the past researcher. So, by simply adjusting the pH from 6 to 12, the Chromium can be precipitate to the bottom of the beaker and then can simply be removed.

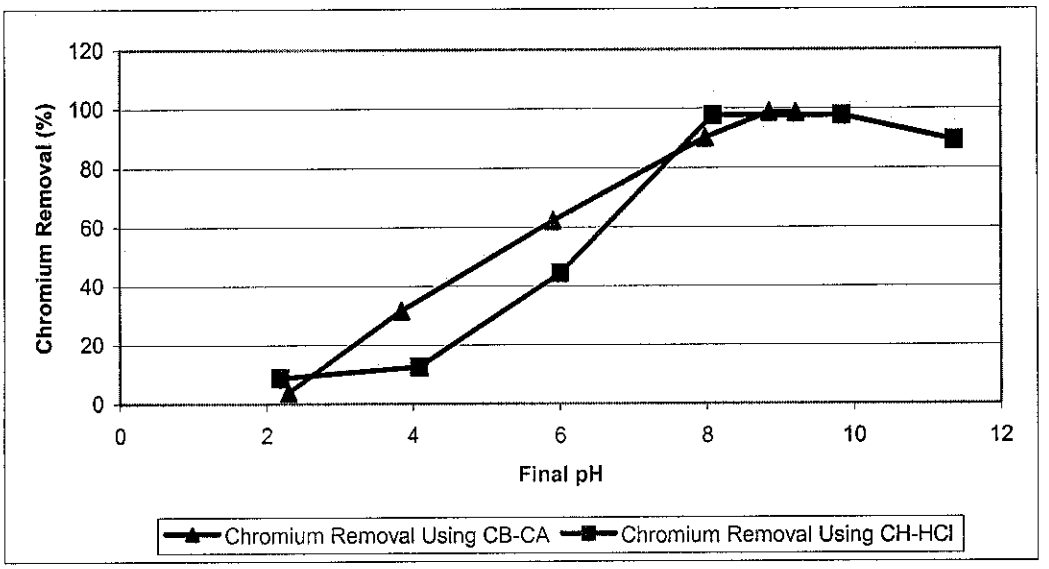

Figure 4.8: Percentage of Chromium removal against final pH.

The graph in Figure 4.8 above shows the Chromium percentage removal using CB solution and Calcium Hydroxide ($Ca(OH)_2$). By comparing those two coagulants, both had removed more than 90% of Chromium metal in the Chromium aqueous solution. The percentage of Chromium removal by CB solution were about 98.8% at pH 8.85 and for Calcium Hydroxide ($Ca(OH)_2$), it had removed about 97.7% at pH of 8.96. This results shows that the CB solution can remove Chromium in the aqueous solution.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

The study has demonstrated that CB-CA solution was capable to remove heavy metal from a solution of 4-20ppm. Higher removal of Copper was achieved at a final pH of 8.1 and for the Zinc removal was achieved at a final pH of 9.03. For Cadmium, the maximum pH of Cadmium removal that can be produced was 9.4. For the last heavy metal that had been experimented was Chromium. The optimum Chromium removal was at pH of 8.85. This implies that the CB-CA solution was an important media in removal process. The percentage of removal of Copper by using CB-CA solution and Calcium Hydroxide ($Ca(OH)_2$) were 96.3% and 97.5% and the percentage of removal zinc using CB-CA solution and Calcium Hydroxide ($Ca(OH)_2$) were 93.3% and 91.8%. The percentage removal for Cadmium were 60% for using CB-CA solution and 79.4% by using Calcium Hydroxide ($Ca(OH)_2$). Last but not least was the Chromium metal. The percentage removal were 98.8% and 97.7% for using CB-CA solution and Calcium Hydroxide ($Ca(OH)_2$) respectively. The results indicate that the presences of hydroxide were beneficial in the removal of heavy metals from water. Thus, CB-CA offers the potential for the low cost effective media for the post treatment of heavy metals from water. Precipitations as metal oxide and probably as metals hydroxide were two of the mechanism that contributed to the removal of metals from water solution.

6. REFERENCES

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APPENDICES

APPENDIX I	: XRF Result
APPENDIX II	: Jar Test Result
APPENDIX III	: AAS Result
APPENDIX IV	: Heavy Metals Aqueous Solution Calculation

APPENDIX I

XRF Result

RF S4 PIONEER SAMPLE REPORTS

CHNICIAN: Mohd Shairul
.IENTS NAME: [illegible]
:PT. : ME /CV /EE /CHE

X-Ray GEN. Status (Bef.): GS 312
X-Ray GEN. Status (after): GS
Actual Duration : 14: 20 MIN

\TE PERFORMED : 02/8/07

Time completed : 10:10 am

\MPLES DETAILS:

IO.	SAMPLE ID	DESCRIPTION	QTY.	EVALUATION	PREP.	REMARK
/	/	SKULL BONE	1pcs.	oxides	wax	OK
		Total:	1pc.			

M= 2.12
W= 3.94

tes:

CLIENTS SIGN

TECH.

2/8/07

ıted by Eval on 22-Aug-2007 10:10:51
ıple :Squidbone220807
ıple measured on 22-Aug-2007 09:53:50

Na2O	MgO	Al2O3	SiO2	P2O5	SO3	Cl
3.9 KCps	1.8 KCps	0.8 KCps	1.7 KCps	0.7 KCps	5.5 KCps	27.5 KCps
1.75 %	0.277 %	0.148 %	0.246 %	0.103 %	0.474 %	2.13 %

K2O	CaO	Fe2O3	CuO	SrO	ZrO2	Re
3.1 KCps	1464.2 KCps	2.5 KCps	3.8 KCps	200.1 KCps	40.0 KCps	18.2 KCps
.132 %	92.8 %	0.00564 %	0.00610 %	0.977 %	0.0224 %	0.705 %

ompton	Rayleigh	Norm.
0.72	1.19	100.00 %

ted by Eval on 22-Aug-2007 10:11:20
ıple :Squidbone220807
ıple measured on 22-Aug-2007 09:53:50

O	Na	Mg	Al	Si	P	S
	3.9 KCps	1.8 KCps	0.8 KCps	1.7 KCps	0.7 KCps	5.5 KCps
27.4 %	1.30 %	0.167 %	0.0783 %	0.115 %	0.0448 %	0.190 %

Cl	K	Ca	Fe	Cu	Sr	Zr
27.5 KCps	3.1 KCps	1464.2 KCps	2.5 KCps	3.8 KCps	200.1 KCps	40.0 KCps
2.13 %	0.109 %	66.3 %	0.00394 %	0.00487 %	0.826 %	0.0166 %

Re	Compton	Rayleigh	Norm.
18.2 KCps			
705 %	0.72	1.19	100.00 %

APPENDIX II

Jar Test Result

Table 1: Jar test result using Cuttlebone as a coagulant

Cuttlebone final pH = 9.28
Key Lime (Citrus Aurantifolia) final pH = 2.32
Volume of Copper solution = 150 mL (measured using cylinder)
INITIAL pH = 3.24 (Copper Solution)

					Final Cu^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**Cuttlebone Volume (ml)**	**Key Lime Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	3	2.86	0	0.1	17.06	16.98	17.1	17.0
2	4	4.14	45	0.0	11.859	11.459	11.375	11.6
3	6	6.06	75	0.0	8.702	10.635	9.501	9.6
4	7	6.95	135	0.0	0.926	1.354	1.303	1.2
5	8	8.04	200	0.0	0.197	0.599	0.302	0.4
6	9	9.00	400	0.0	0.628	0.658	0.637	0.6
				RAW	17.366	17.106	17.171	17.2

Table 2: Jar test result using Calcium Hydroxide as a coagulant

$Ca(OH)_2$ final pH = 12.28
Hydrochloric Acid (0.02mol) final pH = 1.561
Volume of Copper solution = 150 mL (measured using cylinder)
INITIAL pH = 3.10 (Copper Solution)

					Final Cu^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**$Ca(OH)_2$ Volume (ml)**	**HCl Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	2	2.03	0.0	20.00	15.1	15.04	14.92	15.02
2	4	3.92	4.4	0.00	16.08	15.72	15.74	15.85
3	6	6.03	6.1	0.00	14.29	14.13	14.13	14.18
4	8	8.07	16.0	0.00	0.34	0.68	0.71	0.58
5	10	10.01	26.0	0.00	0.5	0.53	0.53	0.52
6	12	11.72	100.0	0.00	0.42	0.44	0.44	0.43
				RAW	17.366	17.106	17.171	17.21

Table 3: Jar test result using Cuttlebone as a coagulant

Cuttlebone final pH = 9.42
Key Lime (Citrus Aurantifolia) final pH = 2.32
Volume of Zinc solution = 150 mL (measured using cylinder)
INITIAL pH = 4.46 (Zinc Solution)

					Final Zn^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**Cuttlebone Volume (ml)**	**Key Lime Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	3	3.00	0	0.09	3.863	3.401	3.377	3.55
2	5	4.87	3	0.01	3.643	3.342	3.343	3.44
3	6	6.06	9	0.00	2.863	3.439	3.28	3.19
4	7	7.04	45	0.00	3.077	3.123	3.108	3.10
5	8	8.54	205	0.00	0.473	0.466	0.459	0.47
6	9	9.03	360	0.00	0.26	0.25	0.283	0.26
				RAW	3.949	3.947	3.954	3.95

Table 4: Jar test result using Calcium Hydroxide as a coagulant

$Ca(OH)_2$ final pH = 11.902
Hydrochloric Acid (0.02mol) final pH = 1.591
Volume of Zinc solution = 150 mL (measured using cylinder)
INITIAL pH = 4.523 (Zinc Solution)

					Final Zn^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**$Ca(OH)_2$ Volume (ml)**	**HCl Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	2	2.07	0.0	40.00	3.634	4.057	4.056	3.92
2	4	4.02	0.0	0.07	3.807	3.371	3.358	3.51
3	6	6.05	0.6	0.00	3.289	3.285	3.331	3.30
4	8	7.96	7.7	0.00	0.737	0.801	0.838	0.79
5	10	9.99	11.7	0.00	0.284	0.348	0.339	0.32
6	12	11.45	70.0	0.00	1.089	0.994	1.046	1.04
				RAW	3.949	3.947	3.954	3.95

Table 5: Jar test result using Cuttlebone as a coagulant

Cuttlebone final pH = 9.398
Key Lime (Citrus Aurantifolia) final pH = 2.32
Volume of Cadmium solution = 150 mL (measured using cylinder)
INITIAL pH = 2.482 (Cadmium Solution)

					Final Cd^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**Cuttlebone Volume (ml)**	**Key Lime Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	2	2.42	0	15.0	6.86	6.88	6.88	6.87
2	4	3.66	100	0.0	5.84	5.83	5.84	5.84
3	6	5.93	130	0.0	4.49	4.65	4.74	4.63
4	7	6.98	160	0.0	4.48	4.46	4.43	4.46
5	8	7.88	200	0.0	3.94	3.99	4.00	3.98
6	9	9.18	400	0.0	2.84	2.82	2.70	2.79
				RAW	7.05	7.05	7.03	7.04

Table 6: Jar test result using Calcium Hydroxide as a coagulant

$Ca(OH)_2$ final pH = 11.787
Hydrochloric Acid (0.02mol) final pH = 1.561
Volume of Cadmium = 150 mL (measured using cylinder)
INITIAL pH = 2.155 (Cadmium Solution)

					Final Cd^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**$Ca(OH)_2$ Volume (ml)**	**HCl Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	2	2.00	0.0	30.0	6.77	6.82	6.84	6.81
2	4	4.08	72.0	0.0	6.28	6.24	6.25	6.26
3	6	5.82	91.0	0.0	6.03	6.05	6.06	6.04
4	8	7.90	107.0	0.0	5.79	5.85	5.85	5.83
5	10	10.03	130.0	0.0	1.38	1.56	1.42	1.45
6	12	11.67	160.0	0.0	2.89	2.93	2.77	2.86
				RAW	7.05	7.05	7.03	7.04

Table 7: Jar test result using Cuttlebone as a coagulant

Cuttlebone final pH = 9.443
Key Lime (Citrus Aurantifolia) final pH = 2.32
Volume of Chromium solution = 150 mL (measured using cylinder)
INITIAL pH = 2.37 (Chromium Solution)

					Final Cr^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**Cuttlebone Volume (ml)**	**Key Lime Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	2	2.30	0	16.0	11.60	11.52	11.54	11.55
2	4	3.84	150	0.0	8.10	8.19	8.35	8.21
3	6	5.91	300	0.0	4.59	4.49	4.51	4.53
4	8	7.98	450	0.0	1.18	1.18	1.17	1.18
5	9	8.85	600	0.0	0.15	0.15	0.15	0.15
6	10	9.21	800	0.0	0.18	0.18	0.17	0.18
				RAW	11.98	12.07	11.98	12.01

Table 8: Jar test result using Calcium Hydroxide as a coagulant

$Ca(OH)_2$ final pH = 12.16
Hydrochloric Acid (0.02mol) final pH = 1.561
Volume of Chromium = 150 mL (measured using cylinder)
INITIAL pH = 2.411 (Chromium Solution)

					Final Cr^{2+} Conc. (After Filtration)			
Jar Number	**Initial pH**	**Final pH after jartest**	**$Ca(OH)_2$ Volume (ml)**	**HCl Volume (ml)**	**First Reading**	**Second Reading**	**Third Reading**	**Average Reading**
1	2	2.19	0	30	10.79	11.02	11.05	10.96
2	4	4.08	55	0	10.61	10.45	10.47	10.51
3	6	6.01	65	0	6.53	6.72	6.77	6.67
4	8	8.09	70	0	0.26	0.27	0.28	0.27
5	10	9.84	81	0	0.28	0.29	0.29	0.29
6	12	11.37	140	0	1.29	1.29	1.28	1.28
				RAW	11.98	12.07	11.98	12.01

APPENDIX III

AAS Result

Cu(324.8nm)

Analyst:
File Comment:

Comment:
Flame

Optics Parameters

Element:	Cu
Socket #:	2
Lamp Current Low(mA):	6
Wavelength(nm):	324.8
Slit Width(nm):	0.5
Lamp Mode:	BGC-D2

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	1.8
Flame Type:	Air-C2H2
Burner Height(mm):	7
Burner Lateral Pos.(pulse):	0
Burner Angle(degree):	0

Measurement Parameters

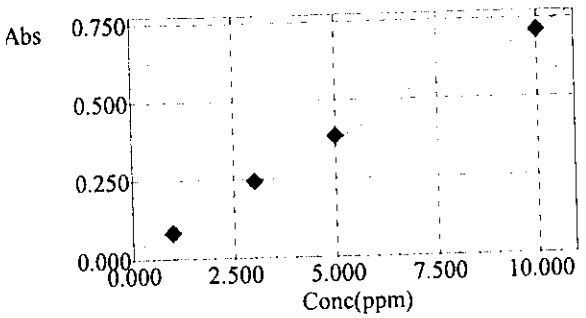
Order:	1st
Zero Intercept:	No
Conc. Unit:	ppm
Repetition Sequence:	SM-M-M-...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num Reps.	Max Reps.	RSD Limit	SD Limit
Blank	2	3	99.00	0.00000
Standard	2	3	5.00	0.00000
Sample	2	3	5.00	0.00000
Reslope	2	3	5.00	0.00000

QA/QC Parameters

QC Type	Judge Calc.	Standard Value	Out of Control Remark

Calibration Curve (C# : 01)

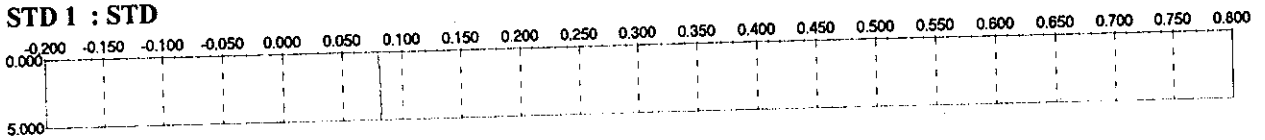


Conc (ppm)	Abs
1.0000	0.0811
3.0000	0.2422
5.0000	0.3849
10.0000	0.7107

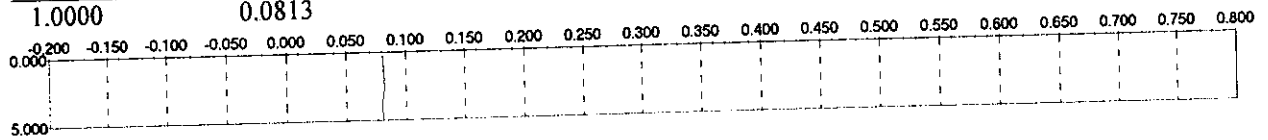
Abs=0.0692609Conc+0.0257358

r=0.9989

STD 1 : STD



True Value		Abs.
1.0000		0.0813

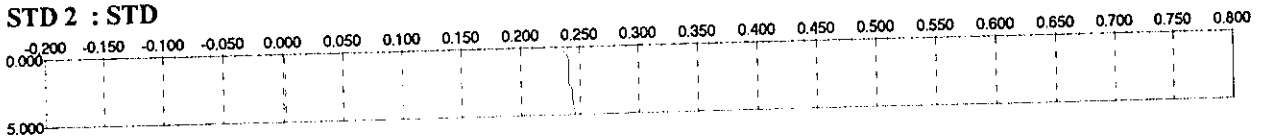


True Value		Abs.
1.0000		0.0809

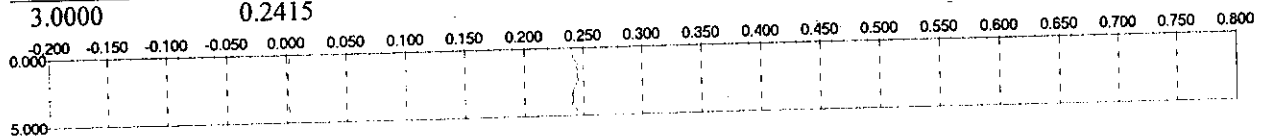
STD 1 : STD Average

True Value		Abs.	Pos.	C#
1.0000		0.0811	R1	01

STD 2 : STD



True Value		Abs.
3.0000		0.2415

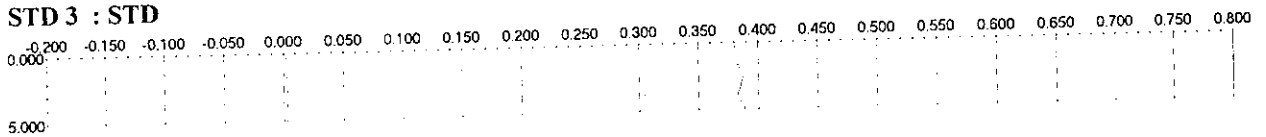


True Value		Abs.
3.0000		0.2428

STD 2 : STD Average

True Value		Abs.	Pos.	C#
3.0000		0.2422	R2	01

STD 3 : STD



True Value		Abs.
5.0000		0.3854

	Sample ID	Cu:Flame Conc.	Cu:Flame Actual
1	001	17.366	ppm
2	002	17.106	ppm
3	003	17.171	ppm
4	004	17.064	ppm
5	005	16.981	ppm
6	006	17.121	ppm
7	007	11.859	ppm
8	008	11.459	ppm
9	009	11.375	ppm
10	010	8.702	ppm
11	011	10.635	ppm
12	012	9.501	ppm
13	013	0.926	ppm
14	014	1.354	ppm
15	015	1.303	ppm
16	016	0.197	ppm
17	017	0.599	ppm
18	018	0.302	ppm
19	019	0.628	ppm
20	020	0.658	ppm
21	021	0.637	ppm
22	022	15.124	ppm
23	023	15.041	ppm
24	024	14.922	ppm
25	025	16.082	ppm
26	026	15.723	ppm
27	027	15.738	ppm
28	028	14.286	ppm
29	029	14.131	ppm
30	030	14.133	ppm
31	031	0.339	ppm
32	032	0.678	ppm
33	033	0.712	ppm
34	034	0.501	ppm
35	035	0.533	ppm
36	036	0.532	ppm
37	037	0.418	ppm
38	038	0.439	ppm
39	039	0.440	ppm

Zn(213.9nm)

Analyst:
File Comment:

Comment:
Flame

Optics Parameters

Element:	Zn
Socket #:	1
Lamp Current Low(mA):	8
Wavelength(nm):	213.9
Slit Width(nm):	0.5
Lamp Mode:	BGC-D2

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	2.0
Flame Type:	Air-C2H2
Burner Height(mm):	7
Burner Lateral Pos.(pulse):	0
Burner Angle(degree):	0

Measurement Parameters

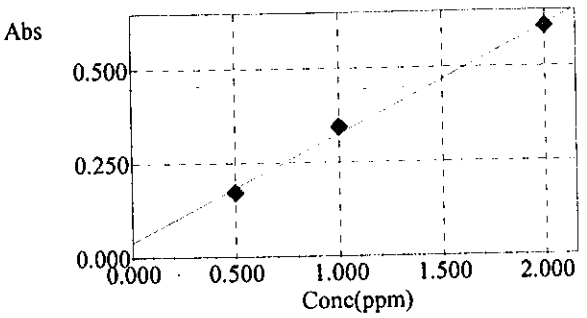
Order:	1st
Zero Intercept:	No
Conc. Unit:	ppm
Repetition Sequence:	SM-M-M-...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num Reps.	Max Reps.	RSD Limit	SD Limit
Blank	2	3	99.00	0.00000
Standard	2	3	5.00	0.00000
Sample	2	3	5.00	0.00000
Reslope	2	3	5.00	0.00000

QA/QC Parameters

QC Type	Judge Calc.	Standard Value	Out of Control Remark

Calibration Curve (C# : 01)

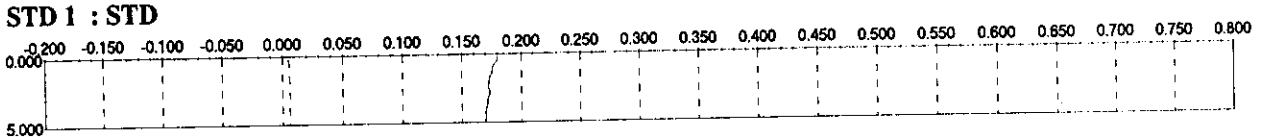


Conc (ppm)	Abs
0.5000	0.1708
1.0000	0.3440
2.0000	0.6054

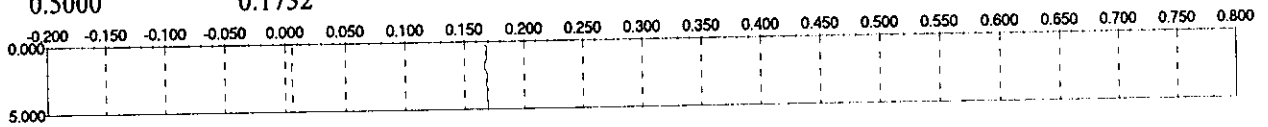
Abs=0.285686Conc+0.0401

r=0.9973

STD 1 : STD



True Value		Abs.
0.5000		0.1732

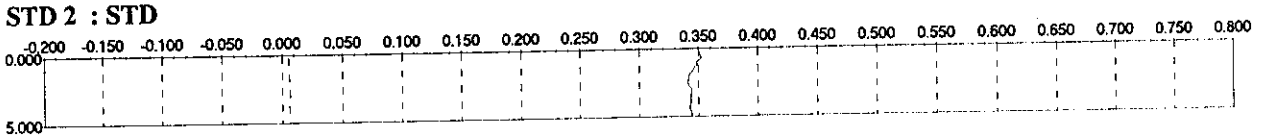


True Value		Abs.
0.5000		0.1685

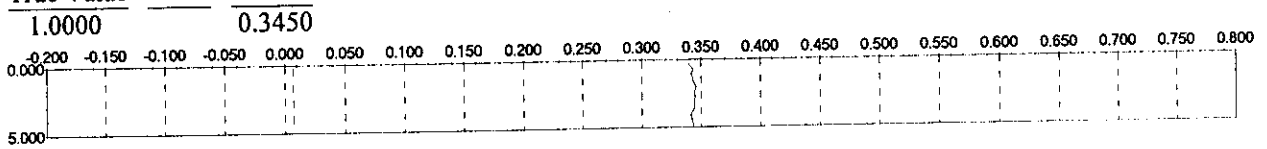
STD 1 : STD Average

True Value		Abs.	Pos.	C#
0.5000		0.1708	R1	01

STD 2 : STD



True Value		Abs.
1.0000		0.3450

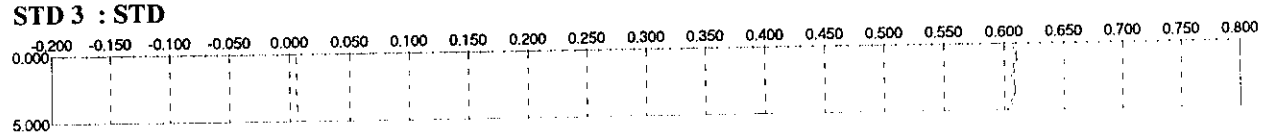


True Value		Abs.
1.0000		0.3431

STD 2 : STD Average

True Value		Abs.	Pos.	C#
1.0000		0.3440	R2	01

STD 3 : STD



True Value		Abs.
2.0000		0.6079

	Sample ID	Zn:Flame Conc.	Zn:Flame Actual
1	001	3.949	ppm
2	002	3.947	ppm
3	003	3.954	ppm
4	004	3.863	ppm
5	005	3.401	ppm
6	006	3.377	ppm
7	007	3.643	ppm
8	008	3.342	ppm
9	009	3.343	ppm
10	010	2.863	ppm
11	011	3.439	ppm
12	012	3.279	ppm
13	013	3.077	ppm
14	014	3.123	ppm
15	015	3.108	ppm
16	016	0.473	ppm
17	017	0.466	ppm
18	018	0.459	ppm
19	019	0.258	ppm
20	020	0.254	ppm
21	021	0.283	ppm
22	022	3.634	ppm
23	023	4.057	ppm
24	024	4.056	ppm
25	025	3.807	ppm
26	026	3.371	ppm
27	027	3.358	ppm
28	028	3.289	ppm
29	029	3.285	ppm
30	030	3.331	ppm
31	031	0.737	ppm
32	032	0.801	ppm
33	033	0.838	ppm
34	034	0.284	ppm
35	035	0.348	ppm
36	036	0.339	ppm
37	037	1.089	ppm
38	038	0.994	ppm
39	039	1.046	ppm

Cd(228.8nm)

Analyst:
File Comment:

Comment:
Flame

Optics Parameters

Element:	Cd
Socket #:	8
Lamp Current Low(mA):	8
Wavelength(nm):	228.8
Slit Width(nm):	1.0
Lamp Mode:	BGC-D2

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	1.8
Flame Type:	Air-C2H2
Burner Height(mm):	7
Burner Lateral Pos.(pulse):	0
Burner Angle(degree):	0

Measurement Parameters

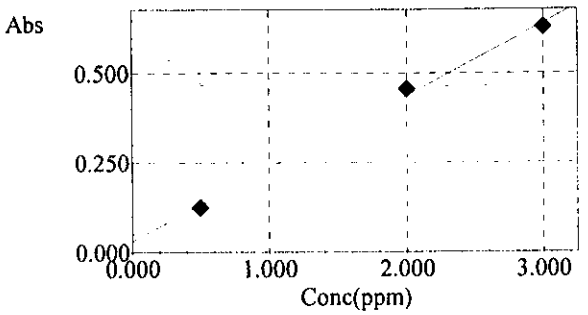
Order:	1st
Zero Intercept:	No
Conc. Unit:	ppm
Repetition Sequence:	SM-M-M-...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num Reps.	Max Reps.	RSD Limit	SD Limit
Blank	2	3	99.00	0.00000
Standard	2	3	5.00	0.00000
Sample	2	3	5.00	0.00000
Reslope	2	3	5.00	0.00000

QA/QC Parameters

QC Type	Judge Calc.	Standard Value	Out of Control Remark

Calibration Curve (C# : 01)

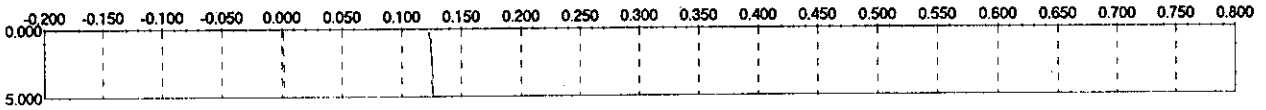


Conc (ppm)	Abs
0.5000	0.1247
2.0000	0.4558
3.0000	0.6296

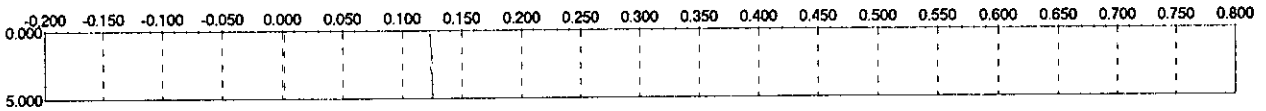
Abs=0.203442Conc+0.0303895

r=0.9980

STD 1 : STD



True Value		Abs.
0.5000		0.1250

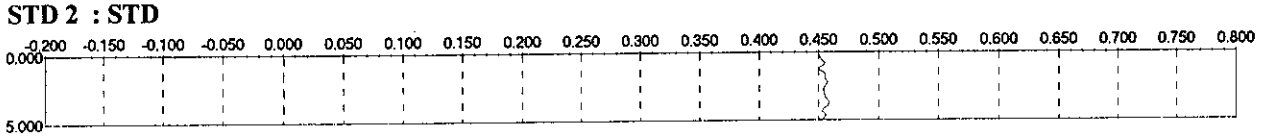


True Value		Abs.
0.5000		0.1244

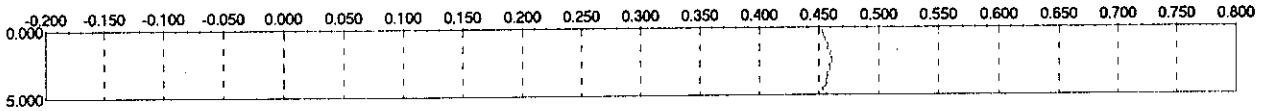
STD 1 : STD Average

True Value		Abs.	Pos.	C#
0.5000		0.1247	R1	01

STD 2 : STD



True Value		Abs.
2.0000		0.4546

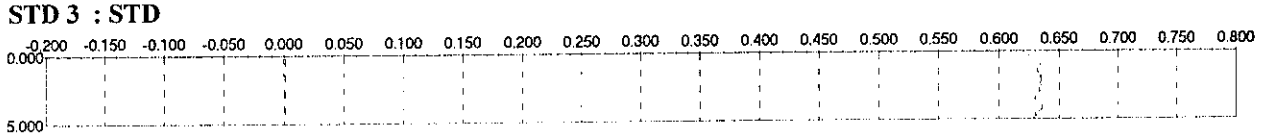


True Value		Abs.
2.0000		0.4570

STD 2 : STD Average

True Value		Abs.	Pos.	C#
2.0000		0.4558	R2	01

STD 3 : STD



True Value		Abs.
3.0000		0.6320

	Sample ID	Cd:Flame Conc.	Cd:Flame Actual
1	001	7.052	ppm
2	002	7.051	ppm
3	003	7.034	ppm
4	004	6.862	ppm
5	005	6.878	ppm
6	006	6.880	ppm
7	007	5.839	ppm
8	008	5.831	ppm
9	009	5.843	ppm
10	010	4.489	ppm
11	011	4.647	ppm
12	012	4.738	ppm
13	013	4.477	ppm
14	014	4.456	ppm
15	015	4.433	ppm
16	016	3.938	ppm
17	017	3.988	ppm
18	018	4.001	ppm
19	019	2.842	ppm
20	020	2.815	ppm
21	021	2.703	ppm
22	022	6.772	ppm
23	023	6.818	ppm
24	024	6.836	ppm
25	025	6.282	ppm
26	026	6.241	ppm
27	027	6.247	ppm
28	028	6.029	ppm
29	029	6.046	ppm
30	030	6.061	ppm
31	031	5.788	ppm
32	032	5.851	ppm
33	033	5.849	ppm
34	034	1.377	ppm
35	035	1.556	ppm
36	036	1.424	ppm
37	037	2.887	ppm
38	038	2.933	ppm
39	039	2.769	ppm

Cr(357.9nm)

Analyst:
File Comment:

Comment:
Flame

Optics Parameters

Element:	Cr
Socket #:	7
Lamp Current Low(mA):	10
Wavelength(nm):	357.9
Slit Width(nm):	0.5
Lamp Mode:	BGC-D2

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	2.8
Flame Type:	Air-C2H2
Burner Height(mm):	9
Burner Lateral Pos.(pulse):	0
Burner Angle(degree):	0

Measurement Parameters

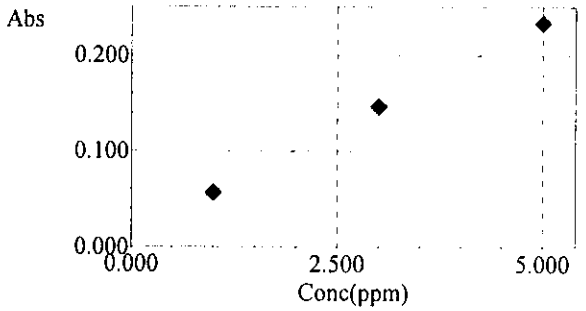
Order:	1st
Zero Intercept:	No
Conc. Unit:	ppm
Repetition Sequence:	SM-M-M-...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num Reps.	Max Reps.	RSD Limit	SD Limit
Blank	2	3	99.00	0.00000
Standard	2	3	5.00	0.00000
Sample	2	3	5.00	0.00000
Reslope	2	3	5.00	0.00000

QA/QC Parameters

QC Type	Judge Calc.	Standard Value	Out of Control Remark

Calibration Curve (C# : 01)

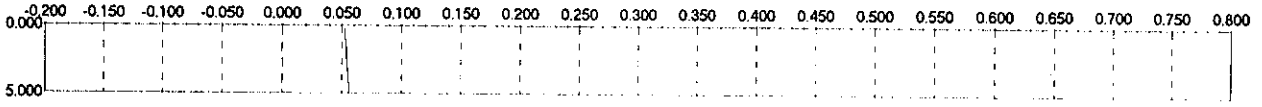


Conc (ppm)	Abs
1.0000	0.0561
3.0000	0.1466
5.0000	0.2329

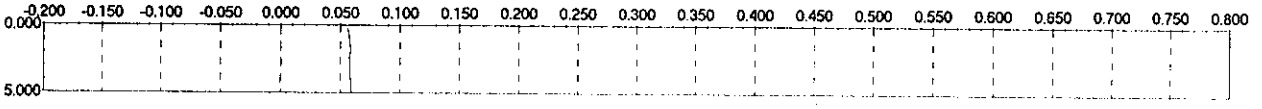
Abs=0.0442Conc+0.0126

r=0.9999

STD 1 : STD



True Value	Abs.
1.0000	0.0543

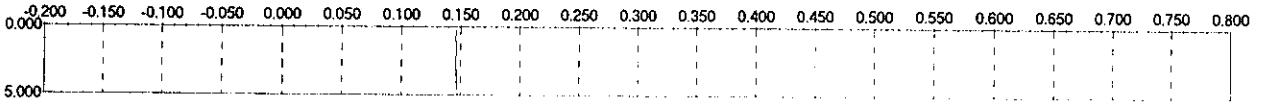


True Value	Abs.
1.0000	0.0579

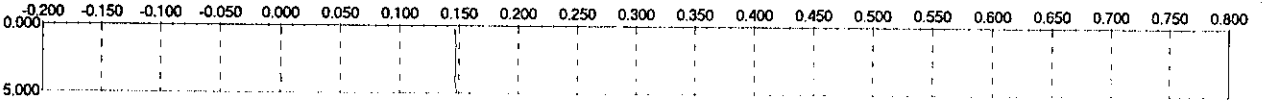
STD 1 : STD Average

True Value	Abs.	Pos.	C#
1.0000	0.0561	R1	01

STD 2 : STD



True Value	Abs.
3.0000	0.1462

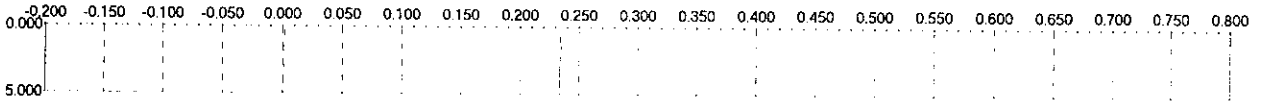


True Value	Abs.
3.0000	0.1470

STD 2 : STD Average

True Value	Abs.	Pos.	C#
3.0000	0.1466	R2	01

STD 3 : STD



True Value	Abs.
5.0000	0.2339

	Sample ID	Cr:Flame Conc.	Cr:Flame Actual
1	001	11.977	ppm
2	002	12.066	ppm
3	003	11.975	ppm
4	004	11.602	ppm
5	005	11.525	ppm
6	006	11.543	ppm
7	007	8.099	ppm
8	008	8.195	ppm
9	009	8.346	ppm
10	010	4.593	ppm
11	011	4.491	ppm
12	012	4.511	ppm
13	013	1.179	ppm
14	014	1.177	ppm
15	015	1.172	ppm
16	016	0.154	ppm
17	017	0.149	ppm
18	018	0.145	ppm
19	019	0.179	ppm
20	020	0.177	ppm
21	021	0.172	ppm
22	022	10.792	ppm
23	023	11.023	ppm
24	024	11.052	ppm
25	025	10.606	ppm
26	026	10.455	ppm
27	027	10.471	ppm
28	028	6.529	ppm
29	029	6.720	ppm
30	030	6.769	ppm
31	031	0.265	ppm
32	032	0.267	ppm
33	033	0.281	ppm
34	034	0.283	ppm
35	035	0.290	ppm
36	036	0.285	ppm
37	037	1.287	ppm
38	038	1.285	ppm
39	039	1.281	ppm

APPENDIX IV

Heavy Metals Aqueous Solution Calculation

Preparation of Copper Solution

The chemical compound of copper nitrate = $Cu(NO_3)_2.3H_2O$

Formula Weight of copper nitrate = 241.60 g/mol

Atomic number of copper nitrate = 63.546 g/mol

$$Cu / mol = \frac{241.60}{63.546}$$

$$= 3.802 \text{ g/mol}$$

1 mol = 1000 ppm

3.802g = 1000 ppm

$$\therefore\ 10 ppm = \frac{3.802}{100}$$

$$= 38.02 \text{ mg/L}$$

For 40 liter of distilled water = 38.02×40

$$= 1520.8 \text{ mg}$$

Preparation of Zinc Solution

The chemical compound of copper nitrate = $ZnCl_2$

Formula Weight of cooper nitrate = 136.28 g/mol

Atomic number of cooper nitrate = 65.409 g/mol

$$Cu/mol = \frac{136.28}{65.409}$$

$$= 2.084 \text{ g/mol}$$

1 mol = 1000 ppm

2.084 = 1000 ppm

$$\therefore\ 10ppm = \frac{2.084}{100}$$

$$= 20.84 \text{ mg/L}$$

For 20 liter of distilled water = 20.84 x 20

= 416.73 mg